

IN-SITU DETECTION AND ANALYSIS OF COAL BED METHANE  
FORMATIONS WITH OPTICAL INSTRUMENTS AND METHODS AND  
APPARATUS TO FACILITATE METHANE PRODUCTION AND  
ANALYSIS

## TECHNICAL FIELD

This invention relates to in-situ methods of measuring or analyzing dissolved, free, or embedded substances with a spectrometer and an apparatus to carry out the method. In particular this invention relates to a method and apparatus of analyzing substances down a well. More particularly, this invention relates to a method and apparatus to detect, analyze and measure methane or related substances in subsurface coal bed formations using a portable optical spectrometer to thereby predict a potential methane production of the well.

## BACKGROUND AND SUMMARY OF THE INVENTION

Coal bed methane is methane that is found in coal seams. Methane is a significant by-product of coalification, the process by which organic matter becomes coal. Such methane may remain in the coal seam or it may move out of the coal seam. If it remains in the coal seam, the methane is typically immobilized on the coal face or in the coal pores and cleat system. Often the coal seams are at or near underground water or aquifers, and coal bed methane production is reliant on manipulation of underground water tables and levels. The underground water often saturates the coal seam where methane is found, and the underground water is often saturated with methane. The methane may be found in aquifers in and around coal seams, whether as a free gas or in the water, adsorbed to the coal or embedded in the coal itself.

Methane is a primary constituent of natural gas. Recovery of coal bed methane can be an economic method for production of natural gas. Such

recovery is now pursued in geologic basins around the world. However, every coal seam that produces coal bed methane has a unique set of reservoir characteristics that determine its economic and technical viability. And those characteristics typically exhibit considerable stratigraphic and lateral variability.

In coal seams, methane is predominantly stored as an immobile, molecularly adsorbed phase within micropores of the bulk coal material. The amount of methane stored in the coal is typically termed the gas content.

Methods of coal bed methane recovery vary from basin to basin and operator to operator. However, a typical recovery strategy is a well is drilled to the coal seam, usually a few hundred to several thousand feet below the surface; casing is set to the seam and cemented in place in order to isolate the water of the coal from that of surrounding strata; the coal is drilled and cleaned; a water pump and gas separation device is installed; and water is removed from the coal seam at a rate appropriate to reduce formation pressure, induce desorption of methane from the coal, and enable production of methane from the well.

Assessment of the economic and technical viability of drilling a coal bed methane well in a particular location in a particular coal seam requires evaluation of a number of reservoir characteristics. Those characteristics include the gas content and storage capability of the coal; the percent gas saturation of the coal; the gas desorption rate and coal density, permeability, and permeability anisotropy; and gas recovery factor.

While industry has developed methods to enhance production from formations that exhibit poor physical characteristics such as permeability and density, currently no practical methods are available to increase the gas content of a coal seam. Thus, identifying coal seams that contain economic amounts of methane is a critical task for the industry. The primary issue in identifying such

coal seams involves developing a method and apparatus to quickly and accurately analyze coal seams for gas content.

Currently accepted methods of measuring gas content involve extracting a sample of the coal from the seam and measuring the amount of gas that subsequently desorbs, either by volume or with a methane gas sensor. However, collection of the coal sample usually changes its gas content to a significant extent before gas desorption is monitored. This degradation of sample integrity leads to degradation of the data collected. That degradation of data creates significant doubt in the results of those common methods. As well, because these methods hinge on waiting for the methane to desorb from the coal, they require inordinate amounts of time and expense before the data is available.

Downhole sensing of chemicals using optical spectroscopy is known for oil wells. For example, Smits et. al., "*In-Situ Optical Fluid Analysis as an Aid to Wireline Formation Sampling*", 1993 SPE 26496, developed an ultraviolet/visible spectrometer that could be placed in a drill string. That spectrometer was incorporated in a formation fluid sampling tool whereby formation fluids could be flowed through the device and analyzed by the spectrometer. That spectrometer was largely insensitive to molecular structure of the samples, although it was capable of measuring color of the liquids and a few vibrational bond resonances. The device only differentiates between the O-H bond in water and the C-H bond in hydrocarbons and correlates the color of the analyte to predict the composition of the analyte. The composition obtained by the device is the phase constituents of the water, gas and hydrocarbons. By correlating observation of gas or not gas with observation of water, hydrocarbon, and/or crude oil, the instrument can distinguish between separate phases, mixed phases, vertical size of phases, etc. By correlating the gas, hydrocarbon, and crude oil indicators, the instrument can presumably indicate if a hydrocarbon phase is gaseous, liquid, crude, or light hydrocarbon. A coal bed methane well

with varying hydrocarbons from coal to methane and, possibly, bacterial material, provides an environment too complex for such a device to differentiate methane and the other substances of interest. The device is not capable of resolving signals from different hydrocarbons to a useful extent, and the device is not capable of accurate measurements needed for coal bed methane wells. Furthermore, the requirements that the sample be fluid, that analysis occur via optical transmission through the sample, and that the sample be examined internal to the device precludes its use for applications such as accurately measuring gas content of coal seams.

In other apparatuses known in U. S. Patent No. 4,802,761 (Bowen et. al.) and U.S. Patent No. 4,892,383 (Klainer, et. al.), a fiber optic probe is positioned to transmit radiation to a chemically filtered cell volume. Fluid samples from the surrounding environment are drawn into the cell through a membrane or other filter. The fiber-optic probe then provides an optical pathway via which optical analysis of the sample volume can be affected. In the method from Bowen et. al., a Raman spectrometer at the wellhead is used to chemically analyze the samples via the fiber optic probe. The method allows purification of downhole fluid samples using chromatographic filters and subsequent analysis of the fluid and its solutes using Raman spectroscopy. However, the stated requirement that the Raman spectrometer be remote from the samples of interest and that it employ fiber-optic transmission devices for excitation and collection ensures that the sensitivity of the device is limited. The device further does not consider the conditions present in subsurface wells when analyzing the samples. Furthermore, as in the Smits et. al. case, the requirements in Bowen et. al. and Klainer et.al. that the sample be fluid and that the sample be examined internal to the device significantly decrease the utility of the device for applications such as measuring gas content of coal seams.

Methods of sample preparation and handling for well tools have been described, as well. In U.S. Patent No. 5,293,931 (Nichols et. al.), an apparatus is disclosed for isolating multiple zones of a well bore. The isolation allows isolated pressure measurements through the well bore or wellhead collection of samples of fluids from various positions in the wellbore. However, such wellhead sample collection degrades sample integrity and does not provide a practical method or apparatus for assessment of gas content in coal seams. The apparatus shown significantly affects any sample collected and is basically a collection device set down a well.

An object of the invention is to provide a method and system to accurately measure substances in wells using optical analysis.

Another object of the invention is to provide a method and measuring system capable of measuring methane in a coal bed methane well.

Another object of the invention is to provide a method and measuring system which utilizes a spectrometer to analyze methane and other substances with emitted, reflected or scattered radiation from the substances and thereby allow a measurement of a side surface of the well.

Another object of the invention is to provide a method and measuring system to accurately measure a concentration of methane in a coal bed methane well and calculate a concentration versus depth for a single well and calculate concentrations versus depth for other wells to thereby predict a potential production of a coal bed methane field.

The objects are achieved by a measuring system for introduction into a well with a housing traversable up and down the well, a guide extending down the well from a fixed location and being operatively connected to the housing, a spectrometer being located inside the housing and including a radiation source, a

sample interface to transmit a radiation from the radiation source to a sample, and a detector to detect a characteristic radiation emitted, reflected or scattered from the sample and to output a signal, and a signal processor to process the signal from the detector and calculate a concentration of a substance in the sample.

Another aspect of the invention is a measuring system for in-situ measurements down a well by a spectrometer. The spectrometer includes a radiation source and a detector. A probe is provided optically connected to the spectrometer and including an optical pathway for transmission of a radiation from the radiation source and at least a second optical pathway for transmission of a characteristic radiation from a sample to the detector. A positioner is provided to position the probe near a side surface of the borehole and to optically couple the optical pathways to the side surface of the borehole, wherein the probe is traversable up and down the well by way of a guide operatively connected to the probe and to a fixed location at the wellhead.

Another aspect of the invention is a method of measuring methane in at least one coal bed methane well. An instrument package is provided in a housing, and the housing is lowered a distance down the well. A radiation source is positioned to irradiate a sample, and a detector is positioned to detect the characteristic radiation from the interaction between the sample and the incident radiation from the radiation source. The sample is irradiated to produce the characteristic radiation. The concentration of methane in the sample is measured by detecting the characteristic radiation with the detector. The detector transmits a signal representative of the concentration of methane to a signal processor, and the signal processor processes the signal to calculate the concentration of methane in the sample.

In another aspect of the invention, a method of measuring a side surface of a borehole using optical spectrometers is provided. An optical spectrometer with a radiation source and a detector is provided. The side surface of the borehole is optically connected to the radiation source and the detector. The radiation source irradiates the side surface of the borehole, and the emitted, reflected or scattered characteristic radiation from the side surface of the borehole is collected. The collected characteristic radiation is transmitted to the detector to output or produce a signal. The signal is transmitted to a signal processor and the concentration of a substance on the side surface of the borehole is calculated.

The side surface is usually a solid material such as coal, sandstone, clay or other deposit. The side surface has been affected by the drill bit. The side surface may also have a film of drilling "mud" or some other contaminant (introduced or naturally found) that has been distributed by the drill bit. The measurement system analyzes the surface of that material, or the material is penetrated to analyze its interior. The surface may be treated (i.e. by washing it with water) before being analyzed. The material of interest is characterized along with any other materials adsorbed or absorbed to the material. These could include gases, liquids, or solids. Preferably, the methane adsorbed to the coal surface and in its pores is identified. The amount of methane on the surface and in the pores is measured.

The samples of interest may be a face of the coal seam, the coal itself, a bacterium or bacterial community which may indicate methane, the water in the well, methane entrained in the coal or water, methane dissolved in the water, or free gas. A free gas may be examined in-situ by providing a pressure change to the water or to the coal and collecting the resultant gas by way of a head-space. The sample or substance of interest may be physically, biologically or chemically treated in-situ before measuring to enhance detection or measurement.

The radiation source is of particular concern and is selected depending on the well environment, the substance to be measured and the background of the sample. Coal shows inordinate fluorescence, and often bacteria and other organic material are present near the coal seams. These substances tend to produce fluorescence which interferes with measurements of other substances. Unless the fluorescence is measured, the radiation source and wavelength are selected to minimize these effects. Coal tends to fluoresce between 600 nm and 900 nm with a significant drop in fluorescence under 600 nm. A radiation source which takes into account these ranges is preferred for measuring the methane, especially the methane adsorbed to or embedded in the coal. Thus, the methane signature relative to the other components is maximized. In some instances a signature of the fluorescence is maximized to characterize the methane indirectly.

The measurements lead to establishing a concentration of methane in the coal bed formation and to the potential production or capacity of the coal bed. The methane is analyzed by obtaining through spectrometers a series of spectra representative of scattered, emitted or reflected radiation from methane in the well. The captured spectra are used to determine the concentration at varying depths of methane present in the coal bed formation. The spectra are manipulated and analyzed to produce the concentrations of methane represented in the well. The use of filters which are designed to eliminate or reduce radiation from sources present in the well is needed to accurately determine the methane concentration or other parameters of the coal bed methane well. Other parameters may include a predictor element or compound that is natural or introduced to the coal bed or well. The filters are chosen depending on the chemical which is of interest. Raman spectrometers are used in most testing, however, near infrared lasers and detectors may be employed to avoid the difficulties associated with fluorescence from material or substances in the water



or well. The measuring system in this invention is based on high sensitivity. One factor that is used to maintain high sensitivity of the system is the reduction or elimination of moving parts throughout the measuring system.

A specialized form of Raman spectroscopy allows one to observe directly, in-situ, the adsorption and desorption processes of methane, carbon dioxide, and other gases onto coal. It has become apparent that, in addition to measuring the amount of gas on the coal, this also enables one to infer certain physical and chemical characteristics of the coal seam environment. For example, one can judge coal seam permeability by removing the gas from a local region of the coal (e.g. by reducing the local pressure via pumping aquifer water, by use of sonic devices such as ultrasound probes, localized fluid heating, use of photonic devices such as lasers, etc.), then observing the "repopulation" of the coal surfaces with methane or other evolved substances over time using certain preferred embodiments of the invention (e.g. via measuring analytes in the coal, on the coal, or within the water or air atmosphere) in order to infer permeability or cleating. (The local region of the coal can be isolated using mechanical, physical or chemical means including zone isolation packers, discrete gas diffusion regimes, etc.) Additional physical or chemical characteristics such as pressure, temperature, flow, quantity, and quality of and water, or other fluids and gases can also be monitored as well using Raman spectroscopy or other transducers in order to correlate with and enhance the primary data from the methane spectroscopy. Other sensing technologies such as gamma ray logging, resistance measurement, or flow meter sensing, can be combined upon the same tool platform as the Raman spectrometer, in order to accurately, repeatably, and absolutely correlate the Raman measurements to more traditional well logging criteria.

In another example, the spectrometer instrument can be used to indicate whether a coal was saturated, unsaturated, or partially saturated with adsorbed

gas. This indication can then be used with other coal seam data to predict the amount of water that must be removed (and the rate of that removal) from the coal seam in order begin to produce gas from a well placed in that seam. Such information can be used to track the progress of a well as the reservoir pressure is being released. Several measurements can be obtained to historically map how methane release from the coals relates to the production of methane during the hydrostatic reduction period. Measurements for methane release may be measured due to the spectrometer response on the coals (either due to methane, coal, bubbles or other analyte), concentration of methane in the water or concentration of methane in the headspace. As such, spectral response libraries can be correlated to the amount of water that must be removed in order to study the limit of production potentials.

The spectrometer instrument package can also be used in conjunction with other types of chemical or physical stimuli in order to enhance or broaden the detection mechanism. For example, the spectrometer instrument package can be used to analyze (downhole, at the wellhead, in the drilling fluid effluent stream, in post-drilling hole processing, or in a lab) a fluid (e.g. water, methanol, etc.) that had been used to extract desired chemicals (e.g. methane, bacteria, etc.) from the coal seam. In another example, the instrument package can be used to analyze a coal seam while the seam was heated and/or cooled locally (e.g. until any adsorbed gas evolves into gas or moves outside of the local region). That analysis indicates diffusional characteristics of the methane on the coal, revealing permeability, cleating, rank, and other characteristics of the coal. In another example, the spectrometer may be used to measure spectrophotometric markers such as flourophores, phosphores, or bio agents that fluoresce upon reaction to methane, coal, or other analytes. Such markers may be tracked over various periods to study diffusion, porosity and density functions of the seams. Zone isolation packers may be used to minimize the concentrations of the

markers. Injections of such markers may come from a device external to the spectrometer, or may be naturally occurring in the coal seam or aquifer. The signal from such markers may also be measured with an imaging spectrometer. Such images may change in intensity, color, or clarity as the marker reacts with the surface.

In the preferred embodiments the instrument package includes a Raman spectrometer for measurements. However, the instrument package may instead include another type of spectrometer and/or optical measurement system. These may include other light sources such as arc, incandescent, metal halide, high-intensity discharge, or other lamps, or diode-pumped solid-state, gas, metal vapor, diode, pumped-dye, solid-state, or other lasers at any different, multiple (including multiple simultaneous), or variable frequencies other than, or in addition to, the traditional, monochromatic, Raman spectrometer excitation laser. These other types of systems may also include the use of discrete optical detectors used in combination with single or various combined optical spectral filters. The spectral filters might be based upon any combination of materials, techniques, and technologies, such as optical thin film interference filters; selectively absorbing glass, crystal, ceramic, metal, semiconductor, liquid, gas, or polymer materials; birefringent optical filters; Fabry Perot etalon or other cavity-based interference filters; polarization selective filters; acousto-optical, electro-optical, thermochromic, and electrochromic filters including variable filters; holographic filters; wavelength dispersive filters based upon diffractive and refractive components and materials such as gratings and prisms; and variable optical filters based upon the tilting of interference or diffraction based elements to change the optical angle of incidence.

The spectrometer instrument package measures directly the methane or other gases adsorbed to, or contained within the structure of, coal and other reservoir rocks. This provides a faster and more accurate method of analyzing

core samples of those rocks than the current technique, gas desorption. For example, a core sample could be brought to a lab for immediate analysis of methane content, reducing gas content determination time by months. As well, the gas desorption technique itself produces a "desorption curve" from volumetric data that is used to back-calculate the gas that was present in the core at the start of the analysis. The spectrometer instrument package could be used as a complimentary technique to verify and improve the data used in that analysis instead of just in-situ monitoring and measuring. In another example, the spectrometer could also be used to analyze cuttings during the drilling process, which precludes the expensive coring process. Captured cuttings would be immediately sealed in a spectroscopic cell and analyzed. The cuttings and the headspace of the gas in the spectroscopic cell could be analyzed for determining methane concentrations.

One preferred step in using the instrument package in a wellbore is positioning the tool so that the instrument optical train is at the appropriate distance from the sample. For example, the instrument optical train may be calibrated to provide maximum sensitivity and accuracy when analyzing samples that are one inch outside of the housing, via a sapphire window through which a focused laser beam is passed. However, small changes in the position of the housing could provide substantial changes in the sensitivity or accuracy of the instrument signal. Further, if sensitivity is used as a judge of absolute (not relative) chemical content in the sample, such changes could cause unwanted errors in the data analysis. In order to reduce the contribution of positioning to data credibility, five examples of methods and apparatus are listed, all of which can be used separately or in conjunction.

Example 1: Electro-optics:

Use of an optic with a focal length that can be varied electronically at a fairly high frequency (e.g. more than 1 Hz, preferably more than 1kHz) provides significant benefits. The focal length of the optic is deliberately varied in a wide range as a maximum in signal is observed or the spectral or physical feature of interest is detected. That maximum in signal is then assumed to be the point at which the sample is located. The optics are then set to that distance and the full analysis performed. This process could be automated using a computer or feedback loop.

Example 2: Optomechanics:

Use of moving optics, either as discrete components, or in combination, to vary the physical location of the focus point of the measurement system relative to a fixed datum, such as the housing of the instrument package or the wellbore. For instance a fiber optic, waveguide, mirror, lens, "integrating sphere", or partial or complete optical assembly could be translated to move the instrument package's focal point relative to a datum. This would not change the numerical aperture of the Raman excitation and collection optical system, as long as no other physical aperture, such as the optical window mount or any housing feature, impedes the optical system's excitation or collection path throughout full range of motion. This can provide constant sensitivity and collection efficiency over a widely varying range of focus point distances relative to a fixed datum. Depending upon the axis of the motion, the optical window in the instrument housing may require re-shaping or enlargement in one or more axes, in order to prevent interference with the optical excitation and collection paths. The focal point may be varied relative to a datum by redirecting the optical axis of a focusing lens, mirror, or system, through the use of a reflective surface, then varying the position of the reflective surface along the original optical axis of the

lens. For instance by placing a mirror at 45 degree angle of incidence to the optical axis of a lens, the optical axis and focal point of the lens is redirected to 90 degrees from it's initial path and location. When the mirror is moved along the original optical axis of the focusing lens, mirror, or system, the resulting focus point translates toward or away from the original optical axis, along an axis normal to the original optical axis, as well as translating away or toward the focusing lens, mirror, or system. This provides some focus scanning capability in an orthogonal direction to the varying focal point distance that is normal to the fixed datum, such as the long axis of the instrument housing or the wellbore. Another arrangement would allow the fixed focal length excitation/collection beam to be optomechanically scanned rotationally, either around the circumference of the wellbore, or vertically along the long axis of the wellbore, through a cylindrical or elongated instrument window geometry, to allow the focus point of the system to be positioned at varying points within the wellbore that are at different distances from the fixed datum of the longitudinal or lateral axis of the instrument housing. The focal point is varied until a maximum in signal is observed or the spectral or physical feature of interest is detected. The required motion may be created by electromechanical, pneumatic, hydraulic, servomotor, gearmotor, piezoelectric, mechanical, thermal expansion, momentum transfer, or gravity-based actuator systems.

Example 3: Extended Beam Waist:

A fixed optic with a deliberately longer focal point is chosen as the "excitation/collection" lens in the instrument optical train. Because of the lens' longer focal point, the laser beam is focused more gradually to a point where divergence begins. In this, the width of the beam at that point is termed the minimum beam waist. In a long focal length lens, the minimum beam waist is more constant along the beam path than for a short focal length lens. Because

the minimum beam waist is more constant, the sensitivity and accuracy of the instrument is less impacted by changes in tool positioning.

Example 4: Collimated Excitation Beam:

A fixed optical excitation system with a collimated light beam is used to stimulate Raman scattering with constant or near constant properties over a highly variable distance between the instrument optical train and the sample to be measured. The collection optical system can be fixed, and designed to have a long depth-of-field, or to be optimized to image an object at infinity, to allow nearly constant collection properties over variable distance. The collection optical system can also be variable, to allow more efficient collection, for instance, by using a larger numerical aperture system with a shorter depth-of-field, and then varying the focal distance by electro-optical or optomechanical means. The excitation and collection optics systems may be co-linear, as in a "180-degree" or "epi" Raman arrangement, and may share one or more optical elements, or the two systems may use separate optics, which are primarily designed for excitation and collection. An example of co-linear, but separate excitation and collection optics, is the use of a collection lens or mirror or detector array with a hole in the collection component to allow a collimated excitation beam to pass through the optic. The excitation and collection optics may also be arranged along different optical axes, which intercept or coincide at the excitation/collection location of the sample to be measured.

Example 5: Internal Standard:

Use of an "internal standard" during analysis provides more benefits. For example, this standard may include naturally occurring materials such as coal, water, or other chemicals. It could also include artificial standards such as injected chemical fluids, mechanically attached solids, etc. By referencing the strengths of any signals collected to the strengths of the signals from such

standards, the response of the instrument can be normalized to known values, allowing more accurate interpretation of results.

Other examples of internal standards include gas (plasma) discharge lamps, metal halide lamps, arc lamps, light-emitting diodes, light-emitting polymers, fluorescent lamps, or other light emissive devices or materials. Internal standards might employ a light source combined with elements having spectrally varying absorptive, reflective, diffractive, or interference properties. Examples would include holmium-doped glass filters, optical interference filters, and Fabry-Perot etalon filters, and fiber Bragg gratings. These "internal standard" sources of Raman scattering, light emission, or light modification may be coupled into the same optical fiber, or discrete optical elements, that the collection optics use to guide light onto the spectrometer detector or other detector(s). If an optical fiber bundle is used to collect light onto the spectrometer detector or other detector(s), one or more fibers out of the bundle may be separated from the collection optics and used to guide the "internal standard" light to the detector(s).

A small part of the excitation light signal may also be taken from the excitation source, by an optical beamsplitter, for instance, and routed to the spectrometer detector or another detector in order to monitor the intensity or spectral frequency stability. By dividing the measured signal intensity by the source signal, or by determining the difference of the spectral location of the source from the ideal signal, a ratio or difference can be used to correct for variations in source intensity and spectral variations. This source light signal may be coupled to the spectrometer detector or other detector by use of an optical fiber or fibers that are co-located in the collection optics fiber bundle, or by use of discrete optical elements to guide the internal standard light to the detector.



Any "internal standard" could potentially be monitored during all measurements by simultaneously guiding the light from the "internal standard" and the collected Raman signal into the same or different detectors, and observing the superimposed standard signal on the collected measurement signal.

The instrument package also can be used to measure methane and other chemicals of interest dissolved in fluids such as water. These measurements can be used to infer other chemical and physical characteristics in the environment, as well. For example, in a coal seam environment, if the coal is not highly saturated with methane, little or no methane is dissolved in the water. Coals that are not highly saturated with methane typically require substantially more production of water before production of gas can begin. Thus, measuring methane dissolved in water in several wellbores could indicate which of the wells will produce gas with the least production of water. Measuring such components during the depressurization process provides a historical data map for producers. Such information may be used to make critical completion decisions for wells in the same lease area.

Ultrasound can be used to induce microscopic variations in pressure in various media, most notably in liquids. In order to produce methane from a coal seam, substantial water must be produced from that seam in order to reduce the local seam pressure. By inserting an ultrasound transmitter into a well, it is possible to induce desorption of methane from the coal face at lower local seam pressures. This reduces the amount of water production required to produce methane from a coal seam. In another embodiment, such a transmitter may assist in removal of mud, coal fines, and other unwanted materials during cleaning of the well.

Mudcake or other materials on the sidewall of a wellbore can interfere with the instrument measurements. By equipping the instrument package with a fixed mechanical sphere, half-sphere, rhomboid, cone, cylinder, or other such protuberance that is pressed through the interfering materials and that does not significantly reduce the optical excitation/collection process of the instrument, interference from those materials can be minimized. In a preferred embodiment, the fixed piece acts as both a protuberance and as the excitation/collection lens. In another embodiment, ultrasound or another physical method could be used to break down the interfering materials in some cases. In another embodiment, such materials can be penetrated by augers or other mechanical means.

An unexpected result is that the instrument package can be used to measure the symptoms of structural and compositional changes in coal that could be used to infer certain chemical and physical characteristics of the coal and its environment. For example, the instrument package measures a low intensity fluorescence peak from coal when it has adsorbates including water or methane. The instrument measures a high intensity fluorescence peak when those adsorbates are absent. Thus, the measurements clearly indicate when the coal has adsorbates and when it does not. In another example, the instrument could be used to measure the vitrinite reflectance value of the coal, which is widely used as a measure of the "rank", and thus economic value of the coal, in a downhole, in-situ environment. This technique might be used prior to, or in lieu of, traditional, expensive, and risky well core-sampling processes. Information gained from these types of "matrix" measurements can be used to evaluate the economic value of a particular coal formation, to distinguish that coal formation from other coal formations, and to select the desired completion and production methods to use when developing natural gas found in that coal formation.

The instrument package can be used to infer the presence of methane and other adsorbates or changes in the coal substrate by indicating the presence or

absence of other materials. For example, a decrease in certain substrate signature vibrational modes may indicate a loss or gain of adsorbate. In another example, the presence of one adsorbate such as carbon dioxide may indicate the absence of another adsorbate such as methane (and vice versa).

The instrument package can be used to monitor sequestration of certain gases such as carbon dioxide into rocks such as coal. For example, it could be used to observe sequestration metrics for carbon dioxide onto coal including rate of sequestration, extent of sequestration, resulting desorption rate of carbon dioxide from coal, etc.

Internal (e.g. instrument related) and external (e.g. naturally-occurring or injected) standards can be used to normalize instrument throughput, focal length of the excitation/collection optic, laser power, detector response, and dispersion frequency scale.

For wellbore measurements of methane in water, the hydrostatic pressure in the wellhead may play a role in the amount of methane found in the water. An induced variation in the reservoir pressure could indicate changes in the coal-methane-water equilibria and predict the desired conditions for gas production.

Ultrasound treatment can also be used to induce desorption from field samples in the well. Such desorption could act to preconcentrate the methane before the measurement is made. Further, ultrasound treatment may be used to clean sidewalls and other materials in the well in order to pretreat those materials before making the measurement. Finally, ultrasound treatment could be used to clean contaminated windows in the tool without requiring removal of the tool from the well.

In order to reduce optical interference from undesired materials in the environment, such materials may be filtered to remain away from the optical

path with fine nylon or SS mesh screen. Simple diffusion or mechanical siphoning may be used to deliver the desired sample to the relevant measurement region.

Production of methane from coal occurs in part through a natural methanogenic process. Production can occur during the early life cycles of the consortia or may be active to this day. A database that describes how methanogenic bacteria consortia change their gas production rates as a function of environmental variables, including temperature, pressure, water quality, coal rank, permeability, etc. is useful in providing key coal seam statistics.

During coalification, the bacteria consortium likely changes in overall population and relative composition of each type of bacteria. Identification of those total and relative populations (i.e. the life cycle state) allows inference of the reserve history and thus future production potential for a coalbed methane well. Identification requires capturing, isolating and culturing the relevant bacteria responsible for methanogenesis. Several bacteria have been captured and isolated that are responsible for methanogenesis. The capturing, isolation and culturing protocols for these bacteria are known. Utilization of this library of information provides an ability to forecast ideal conditions for methanogenesis.

By understanding how a consortium interacts with its chemical and physical environment, one is able to predict what type of reserves contain economic amounts of gas based on the reserve rock's chemical and physical characteristics. One can also identify conditions favorable to accelerated coalification, thus enabling increased gasification of the coal and potentially extending the life of a coalbed methane well.

Other objects, advantages and novel features of the present invention will become apparent from the following detailed description of the invention when considered in conjunction with the accompanying drawings.

## BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a side plan view of an embodiment of the invention and a coal bed methane well with the spectrometer located at the wellhead and transmission of optical radiation using fibers to a downhole probe;

Figure 2 shows a side plan view of another embodiment of the invention and a coal bed methane well with the spectrometer located in a housing lowered down the well;

Figure 3 shows a sectional view of an embodiment of the housing with a flow passage for liquid or gas analysis;

Figure 4 shows a sectional view of an embodiment of the housing with a non-contacting sample interface;

Figure 5 shows a sectional view of an embodiment of the housing with a head-space for gas analysis;

Figure 6 shows a sectional view of an embodiment of the housing with an off axis sample interface pressing to a side of the borehole;

Figure 7 shows a sectional view of an embodiment of the probe with a fiber optics;

Figure 8 shows a sectional view of an embodiment of the probe with a sample interface pressed against the side of the borehole;

Figure 9 shows a sectional view of an embodiment of the probe with the spectrometer located downhole and a sample interface as a fiber-optic bundle pressed against the side of the borehole;

Figure 10 shows a sectional view of an embodiment of the probe with a flow passage and fiber-optic tip as the sample interface;

Figure 11 shows a sectional view of an embodiment of the probe with a fiber-optic optical pathway;

Figure 12 shows a housing with an ultrasound emitter for cleaning parts of the optical instrument and windows of the housing;

Figure 13 shows a housing equipped with a protruberance to be forced into the coal face;

Figure 14 shows a housing equipped with a heater and pump device to interact with the coal face; and

Figure 15 shows a housing with an ultrasound device which prepares the coal face.

#### DETAILED DESCRIPTION OF THE DRAWINGS

Figure 1 shows a coal bed methane well 1 with a borehole 3 extending from a well head to a coal seam 10 with an aquifer fed water level 9. The spectrometer 4 is located at or near the wellhead and includes a radiation source 5 for producing a radiation to transmit down the borehole 3 to a sample interface 25. The radiation from the radiation source is transmitted by way of at least one optical pathway 7. The sample, in this case being water, interacts with the radiation transmitted from the radiation source 5, and a characteristic radiation for the sample is produced by the interaction. The characteristic radiation is then transmitted by an optical pathway 7 to a detector 6 located in the spectrometer 4 at the surface. A suitable optical pathway 7 for transmission is optical fiber 8. Similar elements are represented by the same reference numeral in the drawings.

The optical fiber 8 extends down the borehole 3 to the housing 12 and feeds into the housing through a high-pressure feed-through jacket 18. The

jacket 18 allows the fiber 8 to enter the housing 12 without subjecting the housing to the conditions down the well, such as high pressure, particles and the water. The housing protects any filter 14 or other instrumentation enclosed by the housing. The fiber 8 may extend out of the housing through another jacket 18 to optically couple the sample or substance of interest. A tip 15 of the fiber 8 supplies the radiation from the radiation source 5 and collects the characteristic radiation.

The optical fiber 8 may be a bundle of fibers where the center fiber transmits the radiation from the radiation source 5 and the other fibers transmit the characteristic radiation. A single collection fiber for the characteristic radiation may also be used. The fiber 8 may also include a lens. The fibers use a polished tip or fused tip.

The sample interface includes an inlet 16 and an outlet 17 for the water in the well. The water flows into the inlet when the housing is positioned down the well at a depth and flows around the tip 15 of the fiber to thereby interact with the radiation from the radiation source 5.

In a preferred embodiment shown in Fig. 2, the spectrometer 4 is located down the well 1 in a housing 12, thus reducing the effects of the long distance transmission of the radiation. The spectrometer 4 is lowered down the borehole 3 by a guide wire 21 to a depth, and the depth is controlled by a guide controller 20 at the surface 2.

This embodiment shows the radiation source 5 providing radiation by an optical pathway 7 which is not a fiber. The radiation is directed to a beam splitter 23 and through a window 24 to interact with the sample or substance of interest. The emitted, reflected or scattered radiation is then transmitted through the window 24 into the interior and through the beam splitter 23 to the detector 6.

In this embodiment, no moving parts are present in the housing 12. This allows for increased sensitivity and accuracy.

The guide wire 21 may be a wireline, a slick line, coiled tubing, drill stem or other type of guide. The guide wire is provided for positioning the housing down the well and may also transmit a signal to a data recorder or other processor at the surface. If the signal is not transmitted by the guide wire, a signal or data storage device is needed in the housing. The guide wire may also furnish electrical power to the instrumentation located in the housing, or a battery may be located in the housing.

Figs. 3-6 show embodiments of the housing 12 with the spectrometer 4 enclosed therein, when used with a guide wire 21. Fig. 3 shows a flow passage for the sample interface where the radiation source 5 provides an incident radiation through a window 24 to interact with water. The characteristic radiation is transmitted through another window 24 to the detector 6. The characteristic radiation passes through filters 14 before the detector 6. The housing 12 itself may be streamlined 26 to provide for smooth passage of the housing down the well.

Fig. 4 shows a housing 12 designed for a non-contacting sample interface at the tip of the housing. Here the radiation source 5 produces radiation which is transmitted by an optical pathway 7 to a reflector or grating 27 to direct the radiation through a window 24 at the tip of the housing. The radiation interacts with the sample or substance of interest a distance away from the window 24. The characteristic radiation is then transmitted through the window 24 and to a reflector or grating 27 to direct the characteristic radiation to the detector 6.

Fig. 5 shows a confocal arrangement for the housing 12. The radiation source 5 provides radiation directed to a beam splitter 23 which reflects the radiation to a lens 30 and through a window 24 into a head-space 31. The



characteristic radiation travels to the beam splitter 23 and to another filter 14 and other lens 30 to the detector 6.

The sample interface includes the head-space 31 which entraps gas produced by a depressurization of water in the flow passage. A plunger 33 or other device is used to depressurize the water. The head-space 31 collects the gas for measurement and analysis. Gates 32 are provided which allow the water to flow into the housing and then isolate the water from the well to allow for depressurization.

Fig. 6 shows an off-axis spectrometer 4 configuration. The radiation source 5 is off-axis from the well and face of the borehole 3. The radiation source 5 provides a radiation down an optical pathway 7 through a lens 30 and window 24 onto a sample or substance of interest. The characteristic radiation travels through the window 24, another lens 30 and a filter 14 to the detector 6. The housing 12 has an adjustable device to press the housing to the side surface of the borehole. An extendable leg 36 is provided that by a controller 37 moves out from the housing 12 and contacts the side surface of the borehole opposite the window 24 and thereby moves the housing 12 towards the opposite side of the borehole. The confocal, off axis and non-contacting optics arrangements may be interchanged.

Figs. 7-11 show embodiments of the housings 12 where fiber optics 8 are employed as at least a portion of the optical pathway 7. Fig. 7 shows a housing 12 as a probe where the spectrometer is not located in the housing. An optical fiber 8 supports the probe and positions the probe along the wellbore. A high-pressure feed-through jacket 18 is used to allow the fiber 8 to enter the housing 12 where filters 14 or other dispersive elements are arranged. The fiber 8 exits the housing and the sample interface is a tip 15 of the fiber 8.

Fig. 8 shows the use of fiber 8 with an adjustable device for pressing the sample interface against the side surface 11 of the wellbore. A bag 40 is expanded by a controller 41 against the opposite side surface of the borehole to thereby press the tip 15 of the fiber 8 against or into the side surface of the borehole.

Fig. 9 shows the use of fibers where the spectrometer 4 is located in the housing 12. The radiation source 5 provides radiation to the fiber 8 which transmits it to the sample by way of a jacket 18. A return fiber 8 is adjacent or abutting the first fiber at the sample interface and extends through the jacket 18 to the detector 6. The housing 12 also has an extendable leg 36 and controller 37 for pressing the housing 12 to the side surface 11.

Fig. 10 shows a fiber optic extending down the well and entering a housing 12 with a flow passage. A filter 14 or other dispersive elements are enclosed in the housing 12 and protected from the well environment. The fiber-optic tip 15 protrudes through a jacket 18 into the flow passage. The flow passage includes an inlet 16 with a filter 45 to filter particulates and other entrained material in the water and an outlet 17.

Fig. 11 shows a fiber 8 optical pathway which enters the housing 12 and provides the transmitted radiation to a filter 14 or other dispersive element, lens 30 and window 24.

Optical spectrometers of utility for this method include, but are not limited to, Raman spectrometers, Fourier Transform Raman spectrometers, infrared (IR) spectrometers, Fourier Transform infrared spectrometers, near and far infrared spectrometers, Fourier Transform near and far infrared spectrometers, ultraviolet and visible absorption spectrometers, fluorescence spectrometers, and X-Ray spectrometers. All other spectroscopies which operate by observing the interactions and/or consequences of the interactions between

naturally-occurring, deliberately-induced, and/or accidentally-induced light and matter are also of utility for this method.

For the spectrometer employing reflected, emitted or scattered characteristic radiation, a Raman spectrometer, a near IR spectrometer, a IR spectrometer, a UV/Vis spectrometer or fluorimeter is suitable for characterizing the side surface of the borehole.

Previously, using spectrometers to measure dissolved methane in water or embedded methane at a remote location like a wellhead was not thought possible. With the advent of portable and inexpensive yet highly accurate spectrometers, the measurement of dissolved methane in water is possible. In some cases the spectrum used to analyze the material of interest may be obscured or blocked to some extent by the medium in which it is found. In the case of coal bed methane, the water and entrained particles may cause significant interference with any measurement of the dissolved or embedded methane. Certain steps may be taken to ensure a more accurate analysis of the methane.

Data correction, filters and steps to improve the signal of the spectrometer and methane may be used to accurately measure the methane concentrations. Methane has a characteristic peak or peaks in the scattered or returned optical spectrum. By adjusting filters and any data correction equipment to the expected methane peak, the dissolved methane may be more accurately measured. Another way of correcting for the interference of water or other entrained material is to adjust or select the wavelength of the radiation used to decrease the effects of the water and entrained material and increase the returned signal due to the methane. The wavelength may also be adjusted or selected to alleviate the effects of the length of the optical pathway. The length of the optical pathway from the spectrometer to the coal bed formation may be

10,000 feet. The great length of pathway will result in increased errors associated with the optical pathway. Means to adjust or correct the laser radiation or returned radiation from the sample may be employed at any location in the measurement system.

In an embodiment of this method, the spectrometers are physically located outside of the water, while sampling probes are introduced into the samples of interest. Such probes provide optical pathways via which interactions between light and matter are observed. In some cases, such probes also deliver the photons which interact with the matter. The probes used may have a lens to focus the source or characteristic radiation or filters to adjust the return spectrum radiation for any flaws in the system or extraneous signals. The probes may need armoring or other means for protecting the probe due to the pressure and other conditions of the well. The optical pathway or fiber optics may also need protection from the conditions of the well.

When the probe is located extreme distances from the spectrometer, such as down a well, corrections must be employed to correct for the inherent errors due to the distance the source radiation and spectrum radiation must travel. One way is to allow for longer periods of sampling in order to receive several spectrums added together to analyze the methane present. Another way is to adjust the signal or radiation through a filter or correction device to allow correction feedback to adjust the return spectrum for flaws and errors associated with the radiation traveling such distances.

In another embodiment of this method, the spectrometers are physically introduced into the water so as to be near the samples of interest. This manifestation provides an unexpected benefit in that delivery of photons to the samples and observation of interactions between light and matter are facilitated by the physical proximity of the spectrometers and the samples.

Both embodiments may also use error correction devices such as dark current subtractions of the return signal to correct for inherent system noise and errors. The systems may also use a technique of calibrating the source radiation and spectrum signal to assure an accurate methane concentration measurement. Such techniques may include data processing for comparing the signals to known spectrum signals. In order to calculate the concentration of methane any of the known techniques of calculating the concentration from a spectrum may be used. A preferred method is partial least squares or PLS to calculate concentrations.

In order to realize a preferred embodiment of this method, it is necessary to interface the spectrometers to the samples of interest. Interfacing the spectrometers and the samples can occur in several ways. Examples of those ways include, but are not limited to: direct optical coupling of the spectrometers and samples using light-guide devices; optical coupling of the spectrometers and chemicals which result from physically treating the samples; optically coupling of the spectrometers and chemicals which result from chemically treating the samples; and optically coupling of the spectrometers and chemicals which result from biologically treating the samples.

One manner of direct optical coupling of the spectrometers and samples using light-guide devices includes, but is not limited to, optical coupling of the interactions between light and matter via fiber optic devices. This manifestation provides an unexpected benefit in that delivery of photons to the samples and observation of interactions between light and matter occur with high throughput directly to the samples in some cases.

A preferred manner of optical coupling is by way of direct transmission of the radiation from the spectrometer to the sample via lenses, filters and/or windows, and the direct transmission of the characteristic radiation from the sample to the detector by way of filters, windows and/or lenses. This reduces the

effects of long distance transmission through fiber optics and facilitates the close proximity of a spectrometer and sample.

The filters used may be placed along the optical pathways of the spectrometer. The filters or dispersive elements, collectively filters, may be wavelength selectors, bandpass filters, notch filters, linear variable filters, dispersive filters, gratings, prisms, transmission gratings, echelle gratings, photoacoustic slits and apertures.

In order for the spectrometers to withstand the conditions particular to wellbores, such as high pressure, low or high temperature, corrosive liquids and dissolved solids, for example, it is preferable to enclose the spectrometers in containers which protect them from such conditions. This novel method provides significant advantages over the prior art in that the enclosed spectrometers can then be introduced directly into the wellbore. This method allows, but does not require, realization of the benefit described by the direct interfacing or coupling of the samples and spectrometers.

In order to interface the spectrometers and the samples using such light-guide devices in the wellbore, it is necessary to design the interface in such a way that is suitable for the conditions particular to sampling environment, such as high pressure, low or high temperature, and dissolved solids, for example. The interface must withstand those and other conditions. One manifestation of such an interface for a fiber optic probe includes, but is not limited to, a high pressure feed-through jacket which interfaces between the conditions present in the enclosed spectrometer and those present in the wellbore. Such a jacket provides significant advantages in that using such a jacket direct optical coupling of the spectrometers to the samples becomes possible.

Methods of achieving optical coupling of the spectrometers and chemicals which result from physically treating samples includes, but is not limited to,

introduction of the samples into a portion of the enclosed spectrometers. That portion is then physically affected so that treatment of the samples is achieved to give a chemical suitable for gas phase analysis via an optical pathway using one or more spectrometers. Such physical treatments include, but are not limited to, depressurization of the samples to release gas into a predefined "head-space" portion of the enclosure. That head space is then analyzed via optical pathways using one or more of the spectrometers. This method provides an unexpected benefit in that gas-phase energy spectra of chemicals are typically comprised of much higher resolution characteristics than the corresponding liquid-phase spectra. Thus, delineation of complex mixtures of gases, such as methane and water, is facilitated using this method.

The water located in the coal bed formation is considered to be stable or at equilibrium. The drilling of the well may agitate the water and may cause clouding or fouling of the water. In some circumstances the effects of the drilling and preparation of the well may be to artificially effect the concentration of the methane in the water and surrounding coal formations. Ways to correct the analyzed water may be employed to more accurately reflect the true methane concentration of the formation at equilibrium. A simple way is to allow the well to come back to an equilibrium after drilling or disturbance. Also, the probe or instrument package that contacts the water in the coal bed formation may be streamlined or controlled to allow for a smooth traverse in the water. The locations of measurement in the well may also alleviate the effects of destabilized water/methane concentrations. By analyzing the water at the top of the formation first, and then continue with measurements down the well will effect the water equilibrium less when measured before traversing the probe or package in the water to be analyzed. A filter may also be used to strain the water or sample.

In order to accurately predict the capacity and the production of a coal bed methane formation by optical analysis, the well must be drilled to an appropriate depth. The depth of the water table, if present, the depth of the top of the coal seam and the bottom of the coal seam are recorded. The well head must be prepared to receive the probe or instrument package. The probe must be coupled to the fiber-optic cable. The fiber-optic cable is coupled to the spectrometer that contains the light source, dispersion element, detector and signal processing equipment and ancillary devices. The computer that serves as an instrument controller, data collection and manipulation device is connected to the spectrometer system. The system (computer, spectrometer, detector and laser) are powered and the laser and operation equipment are allowed to reach an operating temperature. The detector is then cooled to operating temperature. The probe or instrument package is lowered into the well through the well head until the probe or package reaches the water table. The source or laser emits a radiation and the radiation is directed into the optical pathway or fiber-optic cable. The fiber-optic cable transmits the radiation down the well to the probe. The probe emits the radiation onto the sample of interest. The probe may contain a lens or lenses to focus the radiation onto the sample at different distances from the probe. The radiation interacts with the sample and causes the sample to reflect, scatter or emit a signature or characteristic radiation or spectrum. The spectrum or characteristic radiation is transmitted through the probe and optical pathway to the spectrometer. The spectrometer detects the spectrum or characteristic radiation and analyzes the spectrum for characteristic methane peaks or peak. The spectrometer then outputs information to the data processor to be manipulated into information to be used to calculate the concentration and potential production of methane.

During the analysis an initial spectrum is taken at the depth of the water table. The fluorescence is measured and, if the fluorescence is high, the source



radiation wavelength may be adjusted or selected to mitigate the fluorescence. If particulates are present and the noise level from them is high, a different focal length may be chosen to mitigate the noise level. The integration time for the detectors is chosen to maximize the signal. A dark current spectrum is taken with the shutter closed such that no light reaches the detector. The dark current is the noise that is present in the system mostly due to thermal effects. This intensity is subtracted from each spectrum to lower the noise level. The number of co-additions is chosen to balance signal and time constraints. The co-additions will improve the signal to noise but will increase the time for each measurement. The probe or package is lowered to the top of the coal seam and a spectrum is taken. The probe is again lowered and a spectrum is taken at regular intervals of depth until the bottom of the well is reached. The measurements show a concentration of methane in accordance with depth in the well. By correlating the concentration of methane in the well with other data, the capacity of the coal bed formation or seam can be calculated. The probe is then retracted and the well head sealed.

This embodiment of the invention details the technical details surrounding the use of three different optical spectrometer systems capable of identifying and quantitatively analyzing coal bed methane formations. This embodiment centers around development of an instrument package capable of detecting the chemical signatures of dissolved methane and other gases in water and detecting embedded or trapped methane in subsurface coal seams, both from a lowered instrument package and from a fixed monitoring site. Such optic-based instruments are suitable for complex analysis of the physical and chemical properties of dissolved methane and similar formations in the wellbore environments.

In these cases, the instruments themselves are packaged and adapted to the conditions prevalent in these environments, and the formations are

examined in the natural state or after suitable treatment. This provides direct access to the chemistry and geology of the formations to an extent unavailable from core-sampling techniques.

At least three types of spectrometers are suitable for wellbore remote sensing of methane. The first two spectrometers, UV/Vis and near IR, are particularly suitable for "head-space" sensing of gases released after depressurization of the coal bed samples. UV/Vis spectroscopy provides data relating to the molecular absorption properties of the water. Depending on experimental concerns, this data may contain information regarding the identity and concentration of dissolved hydrocarbon gases. Regardless, though, it contains information related to choosing the proper laser excitation wavelength for the Raman spectrometer. Near infrared (NIR) spectroscopy has been widely used to remotely characterize complex gas mixtures. In this case, the NIR spectrometer provides data related to the structure and bonding of the gas samples. If the spectrometer resolution is sufficient, that data contains sufficient information to allow deconvolution of very complex samples.

Both of the above spectrometers require substantial fluid handling to be integrated into the sensor or instrument package. This results in slower collection times and, for the lowered instrument package, a lower spatial resolution for the data, when compared to directly coupled in-situ methods. On the other hand, Raman spectroscopy is performed using state-of-the-art high-pressure probes, allowing rapid chemical analysis of water and methane with no additional hardware.

Raman spectroscopy detects the identity and concentration of dissolved hydrocarbon gases and embedded hydrocarbon gases. The Raman "scattering" of typical materials is quite low, producing significant signal-to-noise problems when using this type of spectroscopy. However, symmetric molecules including

methane show very strong scattering. This moderates signal-to-noise concerns to some extent.

Again, all three spectrometers are refitted to suitable pressure tube specifications. The tube-bound spectrometers will be immersed to suitable depths on available well equipment or located adjacent the well, and the data is collected using existing data translation protocols. The data bandwidth for all three instruments is relatively low – ca. 50 KB per minute is a reasonable rate (dependent to some extent on the signal-to-noise concerns).

#### UV/Vis Spectrometer

Because UV/Vis spectrometers are based on low intensity, white light sources, the use of focused optic probes (such as fiber optics) in this case is not appropriate. Such spectrometers are more suited to gas analysis of the “head space” created after depressurization of a sample. Thus, in order to use the UV/Vis spectrometer for methane analysis, mechanized fluid controls are preferred.

An automated fluid decompression chamber that can be filled, depressurized, analyzed, and evacuated on a continual basis at the well depth of interest is provided. Depressurization of the chamber releases the dissolved hydrocarbon gases into the resultant vacuum where they are efficiently and quickly analyzed by the UV/Vis spectrometer. Evacuation and flushing of the chamber is followed by another cycle.

Some issues of concern using this type of spectrometer are developing the appropriate optical path for analysis, avoiding fouling of the chamber and optical windows by water-borne chemicals and bio-organisms, and establishing the appropriate temperature/pressure conditions for data collection. Corresponding solutions are multiple reflection collection geometries which afford very high

sensitivities, proper introduction of anti-foulants to the chamber during flushing, and laboratory correlation of the entire range of available pressure/temperature collection conditions to resulting data quality.

Doing such head-space analysis also provides a convenient method for the sensor platform to analyze chemically gas bubbles resulting from dissolution, cavitation or mixing, which would not otherwise be suitable for analysis. For example, diversion of captured gas into the head-space through appropriate valves provides the opportunity for direct UV/Vis and NIR analysis of the emitted gases.

#### Near IR Spectrometer

Near IR and Raman spectrometers detect the identity (i.e. molecular bonding) and concentration of dissolved and embedded hydrocarbon gases. Near IR analysis, widely used for quality control in industrial processes, typically gives moderate signals with sufficient information (i.e. overtones of the vibrational bands) to treat very complicated samples. Near IR spectrometers may be used for head-space analysis. Allowing multiple reflections of the beam through the cell (and thus multiple passes of the beam through the sample) provides the unexpected benefit of increasing the signal-to-noise ratio of the data. Direct optical coupling of near IR spectrometers to the samples is also preferred.

#### Raman Spectrometer

Raman spectroscopy is widely used for in-situ analysis of water-borne samples because water does not have a strong interaction with typical Raman laser energies. The Raman spectrometer is based on traditional grating optics, and thus enjoys a high throughput of light.

Spectroscopic capabilities are maximized by, in some cases, using a fiber-optic probe sampling motif based around a filtered, six-around-one fiber-optic probe. The six-around-one fiber-optic probe allows for a safe, fully-sealed optical feed-through from the pressure vessel to the water. This design removes the elaborate fluidics necessary for the other two spectrometers.

Until recently Raman spectroscopy would never have been considered as an in-situ probe due to the large size of available Raman systems and their high power consumption. High efficiency diode lasers and charge-coupled device (CCD) detection, along with better filter technology have made it possible to miniaturize Raman spectrometers and decrease power consumption. Fiber-optic probes have eliminated the complex sampling arrangements that once made Raman spectroscopy difficult and tedious.

A long output wavelength often provides useful spectra from samples that produce interfering fluorescence at lower wavelengths. Even at these longer wavelengths, inorganic vibration shifts that are commonly 400 to 1000  $\text{cm}^{-1}$  wave numbers shifted in wavelength are still near the peak sensitivity of CCD detectors but with the added advantage of a significant reduction in the background fluorescence interference present in many samples. A preferred embodiment uses laser wavelengths which avoid to a reasonable extent any fluorescence characteristic of the sample.

Usually fluorescence is mitigated by providing a laser with a wavelength above the fluorescence. In a preferred embodiment a wavelength of 450 nm to 580 nm is provided from a diode laser. This range is below the wavelength of fluorescence of coal. The shorter wavelength is used to decrease the radiation from the coal and increase the relative radiation from the methane embedded or adsorbed on the coal.

Remote sampling is accomplished in some cases using a six-around-one probe. The epi-illumination probe incorporates one excitation and six collection fibers. This probe allows direct measurement of Raman of dissolved hydrocarbons in water without having to transmit through thick, non-quality optical window ports. High pressure feed-throughs are available for this probe.

Measurements of spectroscopic signatures of water-dissolved hydrocarbons in the laboratory show an energy diagram of the known spectroscopic signature regions of simple hydrocarbons, and the regions interrogated by the three spectrometers considered herein. Thus, all three spectroscopies provide information relevant to the hydrocarbon identity and concentration.

However, the UV/Vis bands typical for these hydrocarbons are NOT strongly characteristic – many compounds absorb in the energy region between 0 and 250 nm. Correlation of the UV/Vis results with those from the Raman and/or near IR leads to detailed chemical analysis. As well, the UV spectrometer must operate in the region where the methane transition occurs.

The detectors used with the spectrometer system are important. To obtain high sensitivity and reduce interference from other substances a CCD type detector is preferred. The charge-coupled device detector allows for only a small portion of the spectrum to be analyzed. Other detectors include photomultiplier tubes, photo-diode arrays, CMOS image sensors, avalanche photo diodes and CIDs.

The measuring system may be supplied with power by the guide wires or by internal batteries.

In order to predict or measure a potential production from a coal bed methane field, a series of wells is measured. Taking measurements of methane

or other substances of interest at a single well and at varying depths down the well provides a concentration of methane versus depth for the well. This indicates the presence and amount of methane in the subsurface zones or strata. By similarly measuring other wells in the coal bed methane formation or field a dimensional plot of methane is obtained. From this the transport of methane, production zones and extent of methane bearing zones is obtained.

Also envisioned for the measurement of the methane or other analytes in the coal or wellbore are other optical instruments which are positioned much the same as the spectrometers. With these instruments, a spectral filter 55 can be used to filter only a portion of the returned spectrum from the sample. This filtered spectrum is then detected and analyzed for the analyte of interest.

As the well and coal bed may become dirty with contaminants both in water and on the coal face after drilling, an ultrasound or other sound wave device 50 is used to clean both the instrument and the coal face. As in figure 12, the device 50 may be located in the housing and produce sound waves which clean the outside or inside of the window 24 or other pieces of the instrumentation. The device 50 located outside the housing or at least able to penetrate the housing as in figure 15 provides that sound waves may be used to clean the window 24 or the coal face to be irradiated. This device may also be used to induce a local pressure change in the methane of the coal to thereby desorb the methane for capture or preconcentration before measurement. In the case of pressure changes a measurement of the sample over time shows the recovery or potential production of the methane. The device 50 can also perturb the coal face to facilitate measurement of analytes.

Another method for changing the local pressure is by way of a pump 53 as in figure 14. The housing shown in figure 14 comprises an outer shell which contacts the coal face and effectively seals the coal face to be measured. Upon

which time the pump may pressurize or depressurize the local area of the shell near the coal face to facilitate measurement. The pump 53 may also introduce markers into this area which due to pressurization flow into the coal bed and interact with an analyte of interest. The pump 53 may then pump out the marker and analyte which may be attached by reaction in order for the optical instrument to measure the analyte or marker within the shell. In a variant the pump 53 may bring the analyte and/or marker into the housing to be measured or analyzed if the optical instrument train is solely contained in the housing. A heater 52 or laser may be used as in figure 14 to heat the local area around the coal face to be analyzed.

As shown in figure 13 the housing may incorporate a protuberance 51 which interacts with the coal face by being pushed into it. The protuberance 51 allows the optical instrument to have a clean or clearer sample to measure if the well bore or coal face are contaminated in some way. The protuberance 51 is pushed into the coal face by mechanical means such as extendable leg 37 acting on another side of the housing. The protuberance 51 may contain portions of the optical train of the optical instrument. The insertion of the protuberance may also affect a certain degree of stability to the housing for measurement or allow positional accuracy for the optical instrument.

Postional accuracy to affect the accuracy and sensitivity of the optical instrument may also be accomplished by way of other means. The optical train or pathway may comprise optics which have a focal length which may be varied electronically, the radiation source may be collimated or an internal standard may be used. Also the optical train may comprise a movable optic 54 as in figure 12. The movable optic or optics 54 vary the focal length and thus allow greater sensitivity and accuracy for measurement.



The foregoing disclosure has been set forth merely to illustrate the invention and is not intended to be limiting. Since modifications of the disclosed embodiments incorporating the spirit and substance of the invention may occur to persons skilled in the art, the invention should be construed to include everything within the scope of the appended claims and equivalents thereof.